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14. ABSTRACT

With the development of the 3D GLSM simulation technique, we could now investigate the effect of a localized mechanical impact on a BZ polymer gel film. Through these studies, we isolated a unique form of mechano-chemical transduction. In particular, we found that a localized impact can drive a system that was initially in the non-oscillatory state into the oscillatory regime. The chemical waves are nucleated in the region of the local impact and propagate outwards. Within the 3D system, these variations in chemical concentration produce

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mechano-chemical transduction

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UU	UU	UU	UU		19b. TELEPHONE NUMBER 412-648-9250

Report Title

Final Report

ABSTRACT

With the development of the 3D GLSM simulation technique, we could now investigate the effect of a localized mechanical impact on a BZ polymer gel film. Through these studies, we isolated a unique form of mechano-chemical transduction. In particular, we found that a localized impact can drive a system that was initially in the non-oscillatory state into the oscillatory regime. The chemical waves are nucleated in the region of the local impact and propagate outwards. Within the 3D system, these variations in chemical concentration produce propagating "ripples" on the surface of the film. We found that these oscillations and ripples depend on the magnitude and location of the applied force. Furthermore, we isolated a remarkable case where the system continues to oscillate even after the applied force is released.

Our results on these 3D systems provide the first predictions that local mechanical deformations can excite traveling chemical waves and wide-spread oscillations within BZ gels. The findings open up the possibility of harnessing BZ gels for a range of applications. Specifically, these materials could be used to create sensors that not only can transmit a signal in response to mechanical impact, but also transport reagents to address the after effects. Since the nature of the oscillations indicates the strength and location of the impact, the coatings could also provide an "early warning system", indicating that the underlying components need to be checked for incipient damage.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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Number of Papers published in peer-reviewed journals: 14.00

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 15.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts: 0.00

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Became a Fellow of the Royal Society of Chemistry

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Olga Kuksenok	0.50
Victor Yashin	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Anna Balazs		No
FTE Equivalent:		
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
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Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

FINAL PROGRESS REPORT

Title: Designing Active Coatings and Multilayer Composites: Harnessing Mechano-chemical Transduction in Responsive Gels; Funding: $364, 000 awarded for July 1, 2007 – July 1, 2010

Polymer gels undergoing the Belousov-Zhabotinsky reaction—the BZ gels—are currently the only known polymer networks to *autonomously* convert chemical energy into mechanical action, i.e., no external stimuli are needed to drive this chemo-mechanical transduction. Our goal was to design systems that harness this unique behavior and thereby exhibit a range of novel functionality. To carry out these studies, we developed a new computational approach for modeling large-scale, three-dimensional deformations in polymer networks[1]. Combining this approach with our previously derived kinetic equations for the BZ reaction in polymers[2,3], we undertook the first three-dimensional simulations of chemo-responsive gels[1]. Below, we describe some of our most recent findings. (Papers resulting from this support are listed at the top of the *Bibliography*.)

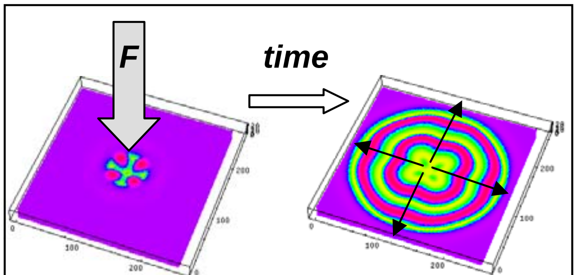

Fig. I Spatially localized force ***F*** drives the BZ gel to oscillate and transmit a global

With the development of the 3D simulation technique, we could now investigate the effect of a localized mechanical impact on a BZ polymer gel film[4]. Through these studies, we isolated a unique form of mechano-chemical transduction. In particular, we found that a localized impact can drive a system that was initially in the non-oscillatory state into the oscillatory regime[3]. The chemical waves are nucleated in the region of the local impact and propagate outwards (see **Fig. I**). Within the 3D system, these variations in chemical concentration produce propagating "ripples" on the surface of the film. We found that these oscillations and ripples depend on the magnitude and location of the applied force. Furthermore, we isolated a remarkable case where the system continues to oscillate even after the applied force is released.

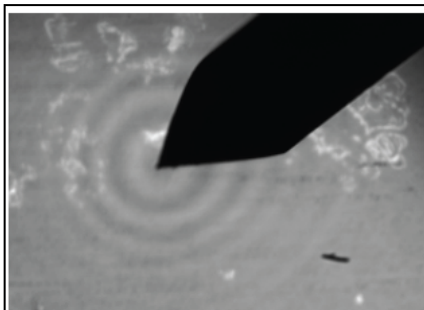

Fig. II. Chemical waves that were produced by mechanically perturbing the surface of a BZ gel using the tip of a needle. Image courtesy of Irving Epstein and Jorge Delgado, Brandeis University (unpublished data).

Our results on these 3D systems provide the first predictions that local mechanical deformations can excite traveling chemical waves and wide-spread oscillations within BZ gels. The findings open up the possibility of harnessing BZ gels for a range of applications. Specifically, these materials could be used to create sensors that not only can transmit a signal in response to mechanical impact, but also transport reagents to address the after effects. Since the nature of the oscillations indicates the strength and location of the impact, the coatings could also provide an "early warning system", indicating that the underlying components need to be checked for incipient damage.

Importantly, Profs. Irv Epstein and Bing Xu at Brandeis University have just obtained what appears to be the first experimental evidence of the mechano-chemical transduction in BZ gels predicted by our simulations (see **Fig. II**). In particular, Xu has fabricated gels that incorporate the BZ catalyst, and Epstein and his postdoc Jorge Delgado have constructed an experimental setup that allows them to observe chemical waves in the gel. These are very preliminary results, and the experiments need considerable refinement. Nevertheless, this is a very promising proof of concept.

As indicated by **Fig. III**, the localized mechanical impact can induce the BZ gels to generate ripples along the surface of the sample[4]. The propagation of these crests and troughs can be harnessed to transport microscopic objects, such as biological cells and synthetic microcapsules, within a microfluidic device or other devices for micro-analysis. In effect, these undulating surfaces could act as “micro-conveyor belts”. By probing the relationships between the features of the mechanical stimuli and the propagating chemical waves, we can facilitate the development of all these various devices.

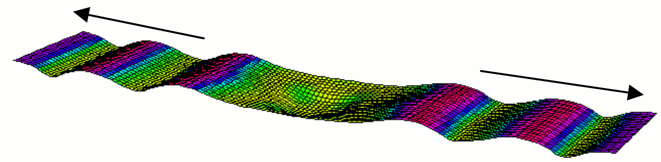

Fig. III. Output from simulations revealing surface ripples (variations in height) along a portion of an oscillating BZ gel. The horizontal arrows mark the direction of the wave propagation.

We note that the BZ reaction is photosensitive and by varying the light intensity, we can manipulate the response of the system. It is this interplay between the chemo-responsive polymer network and the photosensitive reaction that we recently exploited to direct the self-sustained movement of the gels[5,6]. To our knowledge, these are the first computational studies aimed at designing chemo-responsive polymer networks displaying *autonomous* functionality that can be controlled by light. Through these studies, we uncovered novel, nonlinear dynamical phenomena that arise from a coupling of chemical, optical and mechanical energy, and established design rules for creating millimeter-scale devices that effectively operate under their own power to perform valuable functions.

In the above studies[5,6], we focused on long, thin BZ gel filaments. We introduced a light source on the right side of this simulation box. In the presence of this non-uniform illumination, the periodic expansion and contraction of these BZ gels gives rise to a directed motion; **Fig. IV** shows snapshots from the simulations where the expanded regions are highlighted in blue and the contracted areas are marked in red. As can be seen, the pulsating gel moves away from the light source. Once guided along a particular path, the BZ gels will continue to move in that direction, even after the entire sample has left the illuminated region. The results reveal that, on a basic level, these synthetic BZ “worms” exhibit one of the hallmarks of living systems: irritability. In particular, the gels move in response to an adverse environmental condition, which in the context of the BZ reaction is the presence of light.

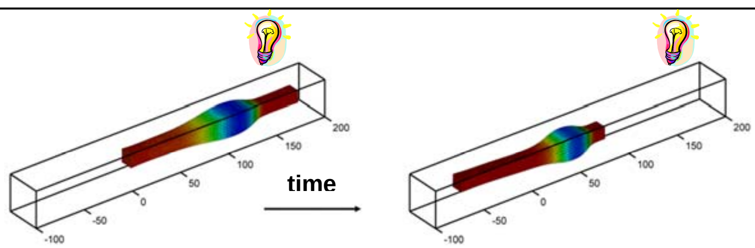

Fig. IV. Motion of a BZ gel “worm” under non-uniform illumination. Through self-sustained oscillations, the sample moves away from the light source.

These simulations reveal that the light can be harnessed not only to direct the movement of a small BZ gel “worm”, but also control the overall morphology of the worm[5,7], as shown in **Fig. V**. Here, the gel can be fashioned into a sigmoidal shape by illuminating only the two ends and keeping the central portion of sample in the dark. The gel effectively reorients to localize within the dark region.

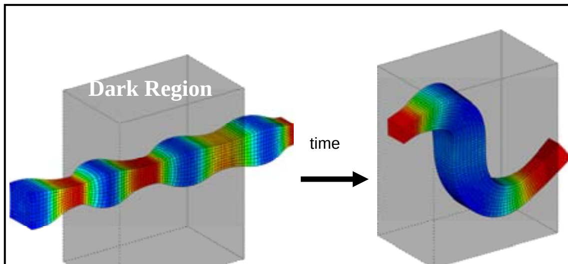

Fig. V. BZ gel worm autonomously reorients to localize within the dark region

These prior studies put us in a unique position to undertake the proposed research, where we will design materials that exhibit a beneficial adaptive mechanism in response to mechanical deformation, undergoing structural changes that enhance the materials’ stiffness or strength.

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